STRUCTURAL STUDIES OF NEW REINFORCING BLACKS FOR LOW TEMPERATURE ELASTOMERS

BY

JACOB FUCHS

B.A., New York University, 1944
M.S., University of Illinois, 1947

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1950

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STRUCTURAL STUDIES OF NEW REINFORCING BLACKS FOR LOW TEMPERATURE ELASTOMERS

Introduction

This investigation was undertaken at the request and with the authorization of the United States Office of Rubber Reserve as part of a comprehensive program to determine the properties and characteristics of new reinforcing blacks which are being compounded into "low temperature" rubber. The most important and the most fundamental problem was to discover that particular property of these carbon blacks which could be correlated with actual reinforcement performance data obtained from actual tests made on rubber containing these blacks. Such correlation, if achieved, would permit immediate prediction of the reinforcement potential of a particular black and consequently remove the necessity for compounding the black into rubber and making actual abrasion tests in order to determine the quality of the reinforced polymer.

Experimental and Discussion

This study utilized the x-ray diffraction technique recently applied to the structural comparisons of some 66 commercial and experimental blacks to evaluate the new reinforcing blacks quantitatively with respect to characteristic interplanar spacings and primary crystallite size and shape (1,2). Using Warren's equations (3), the shape factor, or the ratio of peripheral extension to thickness, L_a/L_c, was calculated for the original samples of black received immediately upon receipt of the samples and then again approximately one year later in order to determine if any significant change took place in the basic structure of the primary crystallites upon long

standing. This information was correlated with actual performance data received from other laboratories cooperating in the Government Tire Test Project sponsored by the Office of Rubber Reserve.

The original x-ray diffraction technique was modified in that an automatic recording North American Philips Geiger-Counter X-Ray Spectrometer was used instead of the conventional photographic type x-ray unit. The use of this instrument permitted a much more rapid and more convenient method of determination of the primary crystallite size and shape since it was no longer necessary to make long exposures, develop the photographic film, and then run the film through a microphotometer in order to obtain a curve from which the desired calculations were to be made.

The type of data obtained from the measurement of the line broadening and the position of the diffracted x-ray beam is illustrated below. Table I summarizes the data obtained from diffraction patterns made immediately upon receipt of the samples. Table II represents the results calculated from patterns made one year later using the same samples.

TABLE I.

Carbon Black	a	c	L_a	L_c	L_a/L_c
Acetylene	2.48	7.14	41.7	22.5	1.85
Kosmobile 77	2.51	7.26	30.7	13.5	2.27
Kosmos 60	2.52	7.34	31.6	13.9	2.27
Philblack 0	2.44	7.40	42.3	13.9	3.05
Statex K	2.47	7.34	38.1	14.3	2.66
Sterling 105	2.50	7.40	35.4	16.1	2.20
Vulcan 2	2.47	7.40	35.0	13.6	2.58

TABLE II.

Carbon Black	a	c	L_a	L_c	L_a/L_c
Acetylene	2.49	7.14	42.2	20.9	2.02
Kosmobile 77	2.53	7.40	30.7	14.3	2.15
Kosmos 60	2.48	7.40	32.4	15.1	2.15
Philblack 0	2.49	7.34	30.8	12.2	2.52
Statex K	2.47	7.28	34.2	14.5	2.36
Sterling 105	2.47	7.40	35.4	16.7	2.12
Vulcan 2	2.47	7.40	38.0	15.4	2.46

Two very important conclusions may be drawn from an examination of these data when these results are examined in conjunction with actual performance data. One conclusion concerns the reinforcement potentials of the various carbon blacks, while the other deals with "aging" phenomena and their effects on the reinforcing ability of the blacks.

Comparison of the L_a/L_c ratios given in Table I with the abrasion ratings of the blacks shows that the abrasion ratings improve as the L_a/L_c ratios become higher. There are definite groupings of the blacks, as regards this ratio, similar to the groupings determined by actual performance tests. That is, Philblack O is rated as the best reinforcing black. It is followed by Vulcan 2 and Statex K, which are both ranked high. Kosmobile 77, Kosmos 60, and Sterling 105 fall into the medium classification, while Acetylene stands alone as being the poorest reinforcing agent. Taking the values of L_a/L_c from Table I, the following results are observed. Philblack O stands alone and far above the other samples with a ratio of 3.05. Statex K and Vulcan 2 have ratios of 2.66 and 2.58 respectively. Kosmos 60, Kosmobile 77, and Sterling 105 are grouped together with values of 2.27, 2.27, and 2.20 respectively. Acetylene exhibits the lowest ratio which is 1.85. It would be rather meaningless to attempt to differentiate between the reinforcing abilities of Kosmos 60, Kosmobile 77, and Sterling 105, for example, since their L_a/L_c ratios are so

close together, but there is no question about the difference between, say, Kosmobile 77 and Statex K. The groupings of the values are spread sufficiently to enable classification of the blacks as excellent, good, mediocre, or poor, and these ratings for the new reinforcing blacks agree with their respective performance ratings.

There is another important consideration in the carbon black-rubber picture, and that is the subject of "aging" and its effect on the reinforcing ability of carbon black. An examination of Tables I and II shows that the L_a/L_c ratios of all the blacks decreased over the period of a year with the exception of Acetylene whose ratio increased. This means that some sort of internal reorganization took place within an electron microscope particle such that, with the exception of Acetylene, all the primary crystallites thickened. The fact that this must be an "internal" phenomenon is shown by the fact that surface adsorption measurements made on "aged" particles give identical results with measurements made on the original samples. Therefore, on the basis of the previous contention that the shape factor is a measure of reinforcing ability, each of these blacks should become poorer reinforcing agents, again with the exception of Acetylene, as time elapses. This theory is borne out by actual performance data submitted by Mandel, Stiehler, and Steel (4). They found that the Wear Indices of tires tested after a few months of shelf-aging definitely increased, with the exception of those of treads made with Acetylene Black, which gave a slightly lower Wear Index. They also found that the relative order of the blacks remained the same for the furnace blacks. The L_a/L_c ratios from Table II align themselves with these results.

In this work it has been demonstrated for the first time that these new active reinforcing blacks possess a decidedly dynamic structure, as clearly indicated by the thickening of primary particles with time. The primary particles themselves may be termed "Embryonic" crystals in view of the mesomorphic character of carbon black, and as is true of any embryo, the primary function is that of growth accompanied

by a lowering of free energy of the solid state. The more active the black (Philblack O) the greater is the tendency to age, and therefore the more dynamic (vibratory, oscillatory) the embryonic structure of a few carbon layers piled haphazardly together. Coupled with this is the parallel trend of the *c* values which measure the separation of these sheets. In graphite this cell dimension is approximately 6.70 A.U. which means a distance of 3.35 A.U. between sheets. In Philblack O *c* is 7.40 A.U. or a distance of 3.70 A.U. between planes, and this value decreases almost in the same order as L_a/L_c, or as the abrasion resistance, to *c* equal to 7.14 A.U., or planar separation of 3.57 A.U. in Acetylene Black. All these factors are consistent with a decidedly active, high energy, dynamic solid state, and this must play a primary role in the effectiveness in bonding the elastomer molecules until the abrasion resistance far exceeds any previously known values for natural or synthetic rubbers with the best available carbon blacks.

Here is a case which simply does not fit into any concept of adsorption on finely divided solid particles. These new blacks do not differ because of electron microscope particle size, variations in adsorption of nitrogen or iodine by these particles, or variations in any other analytical properties commonly used to characterize the individual blacks. The primary x-ray particle does have the variations in shape and fundamental unit cell dimensions which run exactly parallel with abrasion resistance. Thus their integrated effects within and on the surface of the electron microscope particles, the fact that these are "alive" in the sense of continuous change, the fact that highly disorganized matter is trying dynamically to become first two-dimensionally and then three-dimensionally organized — these determine the bonding to polymer molecules.

In producing samples by immediate chilling of the condensed solid from the furnace, and maintaining them at carbon dioxide-snow temperatures, it was the hope to find the first nucleation of carbon atoms and perhaps an even more embryonic and active mesomorphic form than is evident in

fresh commercial samples after usual processing. Only two such sample collections have been possible to date and both have indicated that the first collectible chilled solid has already reached the same state which is observed in the usual commercial samples after some days at room temperature. In the course of these experiments a sample of a new carbon black, Improved Kosmos 60, was examined and found to have an L_a/L_c ratio of 2.87. On the basis of this figure it was predicted that this latest black would be equivalent to Philblack O in reinforcing ability. This prediction was borne out by results of actual performance tests received subsequently. Although the samples of Improved Kosmos 60 were more recent than the specimens of the original blacks in the investigation, evidences of "aging" were observed.

Other efforts will be made to study the initial nucleation of primary particles and their compacting into aggregates of about 300 A.U. each which distinguish the single electron microscope particle. Certainly without measurably changing this particle in apparent size or shape, internal perfecting of primary particles is going on under conditions of great thermal motion. The primary nuclei must have trapped some entirely amorphous material or fragmentary flakelets of carbon atoms; the edges of the primary particles are decidedly tenuous and incomplete with great unsatisfied forces between carbon atoms. The only recourse in such a dynamic, chaotic state is for new layers to form on the pattern of the three or four layers in each primary particle, for the forces forming the hexagons are much greater than those between planes. In so doing in order to make room, the layers are squeezed closer together as the additional layers straighten out the parent layers, and the unit cell dimensions in the *c* direction, with a maximum of 7.40 A.U., decrease toward the limiting value of crystalline graphite, which is never attained until the carbon blacks are heated to such high temperatures (1100-3000° C.) that they graphitize. The temperatures at which the same degree of graphitization are reached may well be another characteristic property of these carbon blacks, though it is

true that all these blacks tend to approach equilibrium values with time.

The question may be asked as to what does the rubber compounding do to the dynamic changes in the carbon blacks observed by themselves. It is unfortunate that there is a serious experimental handicap in producing x-ray patterns of polymer-carbon black mixtures, since the polymer haloes interfere with the resolution of the black interferences which are required for L_a/L_c evaluations. The polymer may be largely extracted by solution in chloroform, though never completely removed from the black. In prior experiments it has been shown that the carbon black used in the rubber mix may be retrieved essentially unchanged. There is some evidence that blending of these new active carbon blacks with low temperature polymers tends to stabilize them. Thus there is probably less dynamic aging in the blend than in the free state.

This study also included some electron microscope investigations of the new reinforcing blacks. In an attempt to isolate single, or at most, just a few particles, a special new dispersion technique was used to mount the specimens. These particles were then "shadow-cast" with palladium and electron micrographs taken. Although electron microscopy is commonly applied in the carbon black field, shadow-cast single particles have never been observed heretofore. This treatment greatly increases the resolution of the smaller particles and makes possible the indirect observation of the thickness of the particles as well as a profile view of them, and gives a good indication of the actual three-dimensional shape of the specimens. Each electron microscope particle is an extremely tight aggregate of primary particles which no one has ever succeeded in breaking down. The crystallites within it are oriented at random and must have voids as well as amorphous material partially surrounding them.

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VITA

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